



# Efficient TiO<sub>2</sub> blocking layer for TiO<sub>2</sub> nanorod arrays-based dye-sensitized solar cells

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## ARTICLE INFO

### Article history:

Received 24 August 2015

Received in revised form 1 July 2016

Accepted 5 July 2016

Available online 7 July 2016

### Keywords:

Titanium dioxide

Nanorods

Peroxo-titanium

Recombination

Blocking layer

Dye-sensitized solar cells

## ABSTRACT

Thin compact titanium dioxide (TiO<sub>2</sub>) blocking layer was chemically deposited on fluorine doped tin oxide (FTO) coated glass substrate using peroxo-titanium complex (PTC) solutions. After that, TiO<sub>2</sub> nanorod (TNR) arrays of different thickness were grown on this TiO<sub>2</sub> film by hydrothermal method. The blocking layer's crystal structure, morphology, and thickness were characterized using X-ray diffraction, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy measurements. XPS analysis revealed that the TiO<sub>2</sub> blocking layer derived from PTC maintains high degree of Ti–O–Ti linkage. These TiO<sub>2</sub> materials were used as the photo-anode in the fabrication of dye-sensitized solar cells (DSSC). TNR arrays-based DSSC of thickness 6.2 μm with TiO<sub>2</sub> blocking layer showed higher photo-electric conversion efficiency of 1.46% compared to devices with similar TNR array of thickness, 6.1 μm without TiO<sub>2</sub> blocking layer (1.19%). The reason can be ascertained from dark photocurrent density–voltage measurements of the devices which reveal that the TiO<sub>2</sub> blocking layer diminishes the dark current arising from reduction of I<sub>3</sub><sup>−</sup> at the FTO/electrolyte interface apparently by blocking direct contact of the redox electrolyte with the FTO layer.

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) nanostructured film is most often believed as versatile building blocks for the construction of dye-sensitized solar cells (DSSC's) [1,2]. In DSSC's, the TiO<sub>2</sub> photo-electrode essentially serves to collect and transport the photo-generated electrons. However, nanoparticle-based DSSCs rely on trap-limited diffusion for electron transport, a slow recombination step that results in lower efficiency. Also the large grain boundaries of TiO<sub>2</sub> nanoparticles lead to fast recombination of the photo-generated electrons with I<sub>3</sub><sup>−</sup> in the electrolyte prior to their collection at the collecting electrode. Hence, to provide uninterrupted transport of photo-generated electrons in TiO<sub>2</sub>, potential applications of one-dimensional (1D) nanostructures such as nanorods [3], nanowires [4], and nanotubes [5] have been demonstrated in DSSCs. It has been proven that the electron transport in 1D nanostructure is several orders of magnitude faster than that in nanoparticles network [6,7]. Nonetheless, the specific surface area of 1D-nanostructured photo-anode is lower than that of nanoparticle-based films of equivalent thickness, which results in low photo-current due to insufficient dye loading. One promising approach to increase the surface area of

1D nanostructure is to increase its length. In this context, several researchers reported thick 1D nanostructure array to fabricate DSSC and achieved high energy conversion efficiency [8,9]. Recently, Wu et al. [10] fabricated DSSCs with 47 μm ultra-long anatase TiO<sub>2</sub> nanowire arrays and achieved a maximum efficiency of 9.4%. Another approach to improve the charge transport properties and collection efficiency is by introducing a TiO<sub>2</sub> layer over the fluorine doped tin oxide (FTO) layer prior to the growth of 1D nanostructure [11–16]. Wei et al. [12] revealed that TiO<sub>2</sub> nanowire arrays grown on TiCl<sub>4</sub> (titanium tetrachloride)-treated substrate own excellent vertical orientation and produce photo-electric conversion efficiency as high as 1.81%. Sun. et al. [13] made an effort to introduce titanate nanosheet thin film as seed layer at the FTO/TiO<sub>2</sub> nanowire arrays interface and achieved a conversion efficiency of 3%. A combination of increased dye loading amount and reduced charge recombination at the FTO/electrolyte interface due to the involvement of titanium nanosheet thin film could contribute significantly to higher conversion efficiency. Jyoti and Mohan [16] prepared anatase TiO<sub>2</sub> nanotubes on anatase TiO<sub>2</sub> blocking layer by simple solvothermal technique and achieved an overall energy conversion efficiency of 7.28%. Recently, Kavan et al. [17] investigated the electrochemical properties of thin compact layers of TiO<sub>2</sub> that were grown by thermal oxidation of Ti by spray pyrolysis, electrochemical deposition, and atomic layer deposition to prevent recombination of electrons from the substrate (FTO or Ti) with a hole-conducting medium at the

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interface. Thus, the TiO<sub>2</sub> blocking layer is essential to maintain high-quality interaction between the interface of TiO<sub>2</sub> and FTO.

In addition, for hydrothermal growth of 1D titanium dioxide nanorod (TNR) arrays, the nucleation site must be uniform and should possess a high degree of crystallinity to avoid any defects during the hydrothermal reaction. Although TiCl<sub>4</sub> plays a favorable role for the deposition of compact layer prior to the growth of nanorod, presence of excess chloride ions could substitute the terminal OH groups on the surface of TiO<sub>2</sub> and could act as defects or impurities in the lattice. Among various methods, like sol-gel used for the preparation of TiO<sub>2</sub> nanoparticles, peroxo-titanium method is found to increase the Ti–O–Ti linkage and minimizes the oxygen vacancy defects. Recently, Qian et al. [18] and Yang et al. [19] derived TiO<sub>2</sub> blocking layers from peroxo-titanium complex (PTC) and studied their effect on dye-sensitized solar cells. An increase in photocurrent due to introduction of PTC overlayer was mainly attributed to the retardation of the back-transport reaction in the FTO/TiO<sub>2</sub> interfaces. In a systematic approach, hereby we made an endeavor to introduce TiO<sub>2</sub> blocking layer using peroxo titanium through chemical bath deposition method over FTO before the growth of TNR arrays and to study the energy conversion effect in DSSC.

## 2. Experimental section

### 2.1. Materials

Fluorine doped tin oxide (FTO) glass plates (sheet resistance 7Ω/sq), lithium iodide (99.9% trace metals basis), iodine (≥99.99% trace metals basis), 4-tert-butyl pyridine (96%) were purchased from Sigma-Aldrich. Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) (Ruthenizer 535-bisTBA), 1-methyl-3-propylimidazolium iodide, platinum electrode (drilled, Cat. No. 74201) and Surlyn polymer frame (Meltonix 1170–25) were purchased from Solaronix. Titanium (IV) chloride was purchased from Merck. All other chemicals used were of analytical grade purchased from Merck and used without further purification.

### 2.2. Electrode preparation

#### 2.2.1. TiO<sub>2</sub> blocking layer

Titanium chloride was chosen as titanium resource for the preparation of stable transparent peroxo-titanium complex solution. Briefly, 0.5 mL of TiCl<sub>4</sub> was dissolved in 50 mL of deionized water under 0–3 °C followed by addition of 2 mL of H<sub>2</sub>O<sub>2</sub>. The mixture turned orange red with addition of H<sub>2</sub>O<sub>2</sub> and turned clear red after stirring for an hour at room temperature. Accordingly, TiCl<sub>4</sub> reacted with H<sub>2</sub>O<sub>2</sub> to form stable PTC solution. Deposition of a layer of TiO<sub>2</sub> was carried out by vertical immersion of FTO substrate in the PTC solution for 12 h under constant stirring at room temperature (25 °C). After the deposition, the substrate was withdrawn from PTC solution and rinsed with distilled water, dried and annealed at 450 °C for 30 min. On calcination, the deposited peroxo titanium complex converted into a uniform layer of TiO<sub>2</sub> over FTO substrate and was designated as FTO<sub>PTC</sub>.

#### 2.2.2. Fabrication of TNR arrays

TiO<sub>2</sub> nanorod arrays were grown on FTO<sub>PTC</sub> substrate using Teflon-lined stainless steel autoclave (45 mL volume, Parr Instrument Co.) following the hydrothermal method reported elsewhere [3]. Briefly, 0.30 mL of titanium (IV) chloride was added to a mixture solution containing 5 mL of deionized water and 5 mL of hydrochloric acid (37 wt%) in a Teflon container and it was stirred for 5 min to allow homogenization. FTO<sub>PTC</sub> glass plates were placed at an angle against the wall of the Teflon-liner with the conducting side facing downwards. The Teflon-liner was in turn placed inside a stainless steel autoclave to initiate the hydrothermal reaction. The reaction was carried out at 150 °C in an electric oven for 4, 8, 12, 20, 30, and

40 h. In a similar way, TNR arrays were also grown on bare FTO. The as-prepared samples were rinsed extensively with deionized water and left to dry in ambient air. Finally, all the samples were annealed at 450 °C for 30 min.

### 2.3. Analytical measurements

X-ray diffraction patterns were recorded using a Bruker D4 Endeavor advance diffractometer with Cu K<sub>α</sub> radiation (1.5418 Å) using a current of 20 mA with an accelerating voltage of 40 kV at a scanning rate of 2°/min. The thickness of as-deposited films was determined using a Dektak XT™ stylus profilometer. Morphology and microstructure analysis of the samples were performed using a JEOL JSM-6380LV scanning electron microscope (SEM), operated at an accelerating voltage of 20 kV. The samples under study were sputtered with gold for 3 min. to obtain a uniform layer of 150 Å thickness using an Edwards S 150 Sputter Coater. The XPS analysis allows studies on the specific bonding configurations in order to monitor the chemical state and the composition of the samples. All samples were subjected to X-ray photoelectron spectroscopy (XPS) analysis (Thermo Scientific Inc. Model K-Alpha) to evaluate the chemical state. The analysis was done with monochromatized Al K<sub>α</sub> radiation (E = 1486.68 eV). The spectral collection was done using scan pass energy of 50 eV with a step of 0.1 eV. The size of the analysis spot was 400 μm. 10 scans with 50 msec dwell time were used for each high-resolution spectral data collection. Ion etching was carried out for 20 s using argon ions accelerated using 2000 V, 16 microampere emission current. The binding energy scale was referenced using standard peaks of Ag or Au and charge compensation during spectral collection was done using a flood gun, in addition to that, all the spectra were corrected using the C1s peak at 284.6 eV of adventitious carbon.

### 2.4. Fabrication of dye-sensitized solar cells

For the fabrication of DSSCs, TNR array electrodes were dipped in dye (Ruthenizer 535-bisTBA) solution ( $3 \times 10^{-4}$  M) in ethanol for 24 h. After the dye adsorption was complete, the electrodes were withdrawn from the solution and dried under a stream of argon. A platinum counter electrode and the dye-coated TiO<sub>2</sub> electrode was then put together with a thin transparent film of Surlyn polymer frame (25 μm). The sandwiched electrodes were tightly held and then heat (130 °C) was applied around the Surlyn frame to seal the two electrodes. A thin layer of electrolyte, consisting of 0.6 M propyl methylimidazolium iodide (PMII), 0.05 M I<sub>2</sub>, 0.1 M LiI, and 0.5 M tert-butylpyridine in 1:1 acetonitrile/valeronitrile, was introduced into the inter-electrode space through predrilled holes from the counter electrode side. The drilled holes were then sealed with a microscope cover slide and finally with a piece of Surlyn to prevent leakage of the electrolyte solution.

### 2.5. Photovoltaic measurements

Solar simulator device (Model: CT80AAA, PET Photo Emission Tech., Inc., USA) consisting of 300 W xenon light source which yields 1 sun AM 1.5G (100 mW/cm<sup>2</sup>) was used to irradiate the whole surface of the test cell. During each measurement, temperature of the platen that holds the cell was maintained at 25 °C using a temperature control system attached to the solar simulator. The power of simulated light was calibrated using a reference silicon photodiode (20 × 20 mm) provided with the instrument. The test cell was placed at the same position as the calibration cell. Photocurrent density–voltage (J–V) plots for all cells were recorded using a Keithley 2400 digital source meter, from +950 to –300 mV in steps of 10 mV.

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